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Data were collected at four U.S. Navy and Marine Corps bases to evaluate bioventing technology efficacy in removing low-volatility fuels from subsurface soils and the groundwater table. These sites have soil contamination attributed to spills or leaks of fuels having low vapor pressures and very low water solubilities, such as JP-5 jet fuel, diesel fuel, #6 fuel oil (bunker fuel), waste oil, and lubricants. The major contaminant studied is JP-5 jet fuel, a kerosene distillate fraction similar to commercial jet fuel A.

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IN SITU REMEDIATION OF LOW-VOLATILITY FUELS USING BIOVENTING TECHNOLOGY

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I. INTRODUCTION

This chapter summarizes data collected at four U.S. Navy and Marine Corps bases to evaluate bioventing technology efficacy in removing low-volatility fuels from subsurface soils and the groundwater table. These sites have soil contamination attributed to spills or leaks of fuels having low vapor pressures and very low water solubilities, such as JP-5 jet fuel, diesel fuel, #6 fuel oil (bunker fuel), waste oil, and lubricants. The major contaminant studied is JP-5 jet fuel, a kerosene distillate fraction similar to commercial jet fuel A. Although most of the data were obtained in the field, laboratory treatability studies are included to clarify field information.

Low-volatility fuels, unlike gasoline-grade fuels, are not removed effectively by soil venting. However, most fuel constituents can be biodegraded under aerobic conditions. The most serious limitations to efficient and complete in situ bioremediation of these fuels and other petroleum hydrocarbons appear to be:

- difficulty aerating contaminated subsurface soils,¹ and
- poor accessibility of the soil microorganisms to the hydrophobic contaminants.²

Aeration of the subsurface is difficult because it takes over three times more oxygen, by weight, than hydrocarbon contaminant to promote complete degradation.³ Thus, use of groundwater as an oxygen carrier becomes impractical because of the poor solubility of oxygen in water. Hydrogen peroxide can provide half its weight as oxygen but it can be toxic or readily degraded by soil microorganisms.⁴⁻⁶

Water-soluble fuel contaminants are rarely toxic to microorganisms because of the low concentrations found in groundwater. This is especially true for low-volatility fuels, which lack significant quantities of the more soluble aromatic compounds found in gasoline. The major components of low-volatility fuels are immiscible in water and thus they remain inaccessible to microorganisms until solubilized or emulsified in the aqueous phase. Emulsification by biosurfactants or synthetic surfactants can be a time-limiting process for in situ bioreclamation because of poor interaction of surfactants with the nonaqueous contaminant phase.^{7,8}

A. Bioventing

In practice, bioventing uses many engineering techniques common to soil venting technology. Both remediation methods are air-driven systems that primarily deal with contamination that resides in the vadose zone soils above the water table. Both techniques can be effective for remediating fuel contamination because insoluble fuel hydrocarbons reside at and above the low groundwater level. However, soil venting cannot cost-effectively remediate soils contaminated with organic compounds having low vapor pressures. By comparison, bioventing should treat all organic compounds capable of biodegrading under aerobic conditions. The desired purpose of bioventing is to promote in situ aerobic biodegradation rather than to vent fuel vapors to ground surface collection or treatment systems. Oxygen can be transported rapidly through water-unsaturated soils, including many with low water permeability (e.g., silts) when low positive or negative pressures are exerted on subsurface soil pores as a result of soil gas extraction and/or air injection. Rapid transport is enabled by the fact that gas diffusion rates are several thousand times those of water and air contains about 25 thousand times more molecular oxygen than aerated water. Vapor transfer through the soil profile, even if not

surface vented, should also increase the surface area in fuel-contaminated soil pores that can be wetted and colonized by hydrocarbon-degrading microorganisms.⁹

Respirometry provides a popular method for measuring aerobic biodegradation rates in soils. This laboratory technique precisely monitors increases in carbon dioxide and/or decreases in oxygen gas levels that result from complete aerobic biodegradation. Using these data, approximate microbial kinetics can be determined. However, soil disturbance or large soil sample variability can often result in laboratory data with little practical value. In situ field respirometry can be used to measure degradation rates in undisturbed, large areas of soil. The technique most often involves measurement of oxygen gas depletion rates following air injection or shutdown of a bioventing system, once atmospheric oxygen concentrations are achieved around soil gas monitoring points. Oxygen depletion rate is generally a more accurate measure of biodegradation rate than carbon dioxide formation, because carbon dioxide can be bound in the soil as carbonates/bicarbonates and is used by many microorganisms as a carbon source for normal microbial biomass production.¹⁰

B. Bioslurping

At many contaminated sites, petroleum contamination is present both in the vadose zone and in the capillary fringe as free product. Regulatory guidelines generally require that free-product recovery take precedence over other remediation technologies, and conventional wisdom has been to complete free product removal activities prior to initiating vadose zone remediation.

"Bioslurping" is a new dynamic technology that teams vacuum-assisted free-product recovery with bioventing to simultaneously recover free-product and remediate the vadose zone. Bioslurping is a

vacuum-enhanced free-phase petroleum (free-product) recovery technology. Unlike other free-product recovery (FPR) technologies, bioslurping systems treat two separate geologic media simultaneously. The systems are designed to extract free-phase fuel from the water table and to aerate vadose zone soils through soil gas vapor extraction. The bioslurper system withdraws groundwater, free product, and soil gas in the same process stream. Groundwater is separated from the free product and is treated (when required) and discharged. Free product is recovered and can be recycled. Soil gas vapor is treated (when required) and discharged.

Bioslurper systems are designed to minimize environmental discharges of groundwater and soil gas. As done in bioventing, bioslurper systems extract soil gas at a low rate to reduce volatilization of contaminants. In most instances, volatile discharges can be kept below treatment action levels. The slurping action of a bioslurper system greatly reduces the volume of groundwater that must be extracted with the free product when compared to conventional FPR systems. High FPR efficiencies are achieved with pressure-induced gradient rather than by the hydraulically induced gradient used by many FPR systems.

II. FUEL CONTAMINATION SITES

Four U.S. Navy sites were evaluated for bioventing efficiency: Fallon Naval Air Station (NAS) in western Nevada, Patuxent River NAS in southern Maryland, Kaneohe Bay Marine Corps Air Station (MCAS) on Oahu in Hawaii, and Twentynine Palms Marine Corps Air Ground Combat Center (MCAGCC) in southern California. At the first three sites, free fuel has reached groundwater, resulting primarily in a horizontal subsurface plume. At Twentynine Palms, because of very deep groundwater and sandy soils, the plumes are primarily vertical.

A. Fallon, Nevada

The Fallon NAS site is located in the high desert, with periodically cold winters and hot summers. The plume being remediated appears to be contaminated solely by rather fresh JP-5 jet fuel from a previously leaking supply pipeline. The subsurface soil consists of mixed fluvial and lacustrine deposits in gradational layers of silt, sand, and clay. The soil profile consists of 2.4 to 3.0 meters of silt with sandy-silt interlayers, underlain by 0.6 to 1.2 meters of silty to clean sand and a thick clay stratum, respectively. The shallow aquifer zone is in the sand layer, and the underlying clay acts as an aquitard. The horizontal fuel plume is confined to the sand layer and lower 0.6 meter of the overlying silt layer. The 0.4-hectare bioventing system is constructed within the 2.8- to 3.2-hectare hydrocarbon plume (see Figure 1). Ambient temperatures in the contaminant zone fluctuate between 12 and 18°C. The groundwater is alkaline and basic (pH 8.9) and of brackish salinity (23 mmho/cm conductivity). Arsenic is a natural contaminant, with concentrations as high as 4 mg/L.

Initial feasibility studies, including soil in situ respiration testing, were conducted in the summer of 1990; the bioslurping system was designed and constructed mainly during late 1991. The system was started up initially in November 1991 but was not run full time until January 1993.

B. Patuxent River, Maryland

The Patuxent River NAS site is situated in upland forested terrain close to Chesapeake Bay. Contamination is predominantly aged JP-5 jet fuel, but less aged gasoline-grade fuel was observed in parts of the hydrocarbon-contaminated soil. The subsurface consists predominantly of mixed fine to coarse fluvial sand, with some thin, discontinuous interbeds of silt and clay that formed in an ice age backwater salt marsh. In some areas thin peat strata exist. The water table and free fuel lie generally

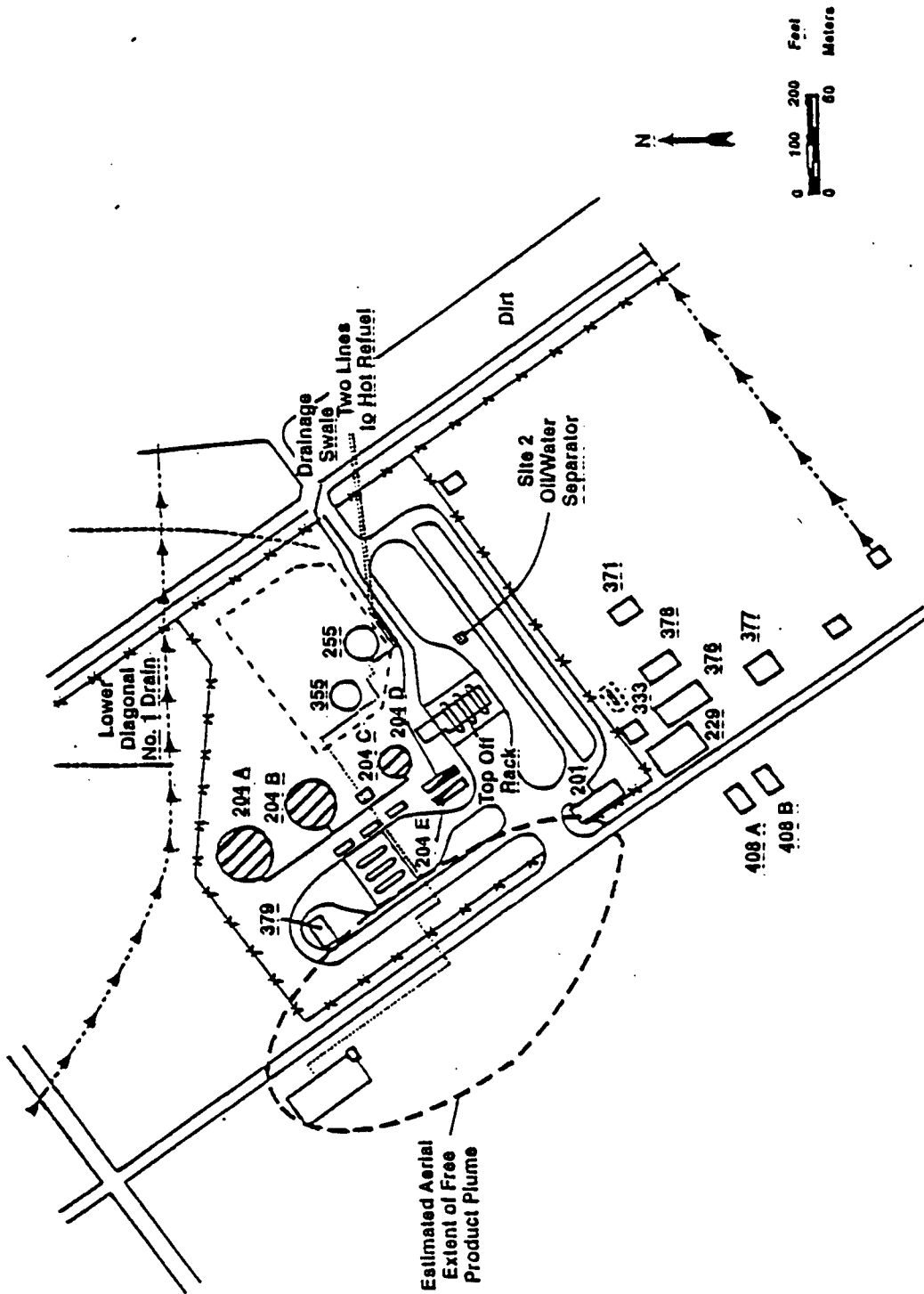


Figure 1. Estimated Aerial Extent of JP-5 Free Product Plume West of NAS New Fuel Farm. Bioslurper System will treat an approximate 0.4-hectare plot within plume.

at depths of 4.3 to 5.5 meters with an extensive clay layer at depths of 6.7 to 7.6 meters serving as the shallow aquifer aquitard. In general, the fuel does not contact the peat layers except near where fuel seeps from a steep embankment along a creek. The groundwater is slightly acidic and is low in dissolved solids (150 mg/L) and salinity (<0.5 mmho/cm, conductivity); temperatures fluctuate between 15° and 20°C. Groundwater and fuel migration patterns are strongly affected by soil fill deposited in shallow canyons that existed prior to underground tank construction.

Vent wells and monitoring points were installed in three phases from the summer of 1987 to the fall of 1990 over an area of about 28 hectares. The contaminant plumes, originating from several sources, cover an area of about 12 hectares. Extensive laboratory and field treatability and feasibility studies were conducted during the well installation period. Laboratory studies included evaluation of synthetic surfactants, JP-5 soil venting rates, biodegradation rates of individual hydrocarbons in fuel-contaminated soils (radiolabel studies), and fuel degradation rates; microbial characterizations; and large soil column evaluations of different nutrient additions and aeration techniques. Field studies included comparative analyses of soil gas and groundwater data, other geophysical evaluations, tracer studies, and geochemical evaluations. In situ respirometry was conducted during the summer of 1990. A bioventing system has not yet been planned for this site.

C. Kaneohe Bay, Hawaii

The Kaneohe Bay MCAS site is located on the Mokapu peninsula surrounded by embayments in a tropical setting with very uniform seasonal temperatures. The contaminant plume is JP-5 jet fuel and it covers nearly 2 hectares around a previously leaking, very large aboveground tank. The subsurface soil profile consists of sand, silt, and clay originating from basalts; basic volcanic tuff; and coral

limestone. The upper section consists predominantly of silty reddish brown sand 0.3 to 4.5 meters thick. This is underlain by a cohesive sandy clay zone that extends to about 6 meters below ground surface (BGS), at the groundwater table. Highly permeable sand and silty sand is encountered below the groundwater table to about 10 meters BGS, where sandy clay and calcareous fines are encountered as the possible aquitard. The fuel appears to reside both in the low-permeability zone above and the high-permeability zone just below the water table. The groundwater appears to be fresh and unaffected by tides.

During previous investigations, nearly 100 soil borings were emplaced at the field site to delineate the extent of the free-product plume. Soil gas monitoring points were installed in August, 1993 and soil samples were collected from three borings for chemical analysis. In situ respirometry was performed following monitoring point installation. Construction of a bioventing system over the entire contaminant plume is scheduled for late 1993, with startup in early 1994.

D. Twentynine Palms, California

The Twentynine Palms Marine Corps Air Station includes numerous small and large spill sites of different types of fuels. The major spills are JP-5 and diesel, but #6 fuel oil, gasoline, and waste oil spills all need to be treated in situ. Approximately 12 sites are planned for bioventing studies. Two of these are detailed field demonstrations at sites contaminated with JP-5 and #6 fuel oil. The remaining approximately 10 sites will be used for pilot-scale bioventing studies.

The subsurface soils at most spill locations consist of rather uniformly graded fine to medium aeolian sand, with few low-permeability interbeds. Because the groundwater table is at 61 to 67 meters, most

fuel plumes are vertical. At one location, preliminary data indicate that a mixed fuel plume has reached the saline groundwater. The #6 fuel oil demonstration site shows contamination more than 14 meters deep.

Vent well and monitoring point installations commenced in March 1993. Initiation of pilot bioventing system operation was expected before the end of 1993 with commencement of the field demonstrations in early 1994. Air permeability testing was initiated during the summer of 1993.

III. METHODS: LABORATORY TREATABILITY STUDIES

A. Effects of Fuel Concentrations on Biodegradation Rates

The effects of total petroleum hydrocarbon (TPH) concentrations on the microbiological degradation of JP-5 contaminated soils was investigated in sealed 40-mL borosilicate volatile organic analysis (VOA) vials. Soil samples collected from the Patuxent River fuel farm were passed through a No. 4 (475 μ m) sieve to remove rocks and to obtain a homogeneous sample. To investigate the effect of concentration, the contaminated soil was mixed with uncontaminated silica sand to provide soil concentrations of 180, 490, 830, and 1,570 mg/kg TPH dry weight soil. Then 15 grams of soil were placed in the 40-mL vials. The vials were closed with Teflon™ septa caps and 20 mL nutrient solution (Restore 375) containing 200 mg/L stabilized hydrogen peroxide (IT Corporation), 400 mg/L ammonium-nitrogen, and 20 mg/L orthophosphate-phosphorus was added to each vial. Each treatment per sampling time was replicated in triplicate and the experiment was run for 120 days on an orbital shaker at 20°C. The ammonium concentrations and pH were kept uniform, and the soil-water dissolved oxygen levels were maintained at greater than 3 mg/L by adding hydrogen peroxide through the Teflon™ septa when necessary. The content of each respective bottle was analyzed for

TPH by the EPA Modified 8015 Method with methylene chloride extraction. Heterotrophic bacteria counts were determined by serial dilution and plating on solid media after incubation at 37°C for 36 hours.¹¹ Other analyses included soil-water dissolved oxygen, pH, ammonia-nitrogen, nitrate-nitrogen, nitrite-nitrogen, and phosphate-phosphorus.

IV. METHODS: FIELD STUDIES

A. Soil Gas Permeability and Radius of Influence

An estimate of the soil's permeability to fluid flow (k) and a determination of the radius of influence (R_i) of the vent wells provide important factors to consider in bioventing system design. On-site testing gives the most accurate estimate of the soil gas permeability, k . On-site testing also can be used to determine the radius of influence that can be achieved for a given well configuration and its flow rate and air pressure. These data are used to design full-scale systems with regard to spacing the vent wells, sizing the blower equipment, and ensuring that the entire site receives a supply of oxygen-rich air to sustain in situ biodegradation.

Soil gas permeability, i.e., as a soil's capacity for fluid flow, varies according to grain size, soil uniformity, porosity, and moisture content. The value of k is a physical property of the soil; k does not change with different extraction/injection rates or different pressure levels. Soil gas permeability generally is expressed in the units cm^2 or darcy ($1 \text{ darcy} = 1 \times 10^{-8} \text{ cm}^2$). As with hydraulic conductivity, soil gas permeability may vary by more than 1 order of magnitude on the same site due to soil variability.

The radius of influence is defined as the maximum distance from the air extraction or injection well where measurable vacuum or pressure (soil gas movement) occurs. R_i , a function of soil properties, also depends on the configuration of the venting well and extraction or injection flow rates, and is altered by soil stratification. At sites with highly permeable soils, pressure monitoring alone may not be adequate to estimate R_i for bioventing. At these sites the lack of resistance to air flow will reduce the injection pressure. It is best to monitor changes in soil gas composition, particularly increases in oxygen concentration at oxygen-deficient sites, or to use an inert tracer (i.e., helium) to observe the radius of influence. A detailed description of the air permeability test procedure is presented in Hinchee, et al.¹²

B. In Situ Respiration Testing

The in situ respiration test consists of placing narrowly screened soil gas monitoring points into the unsaturated zone fuel-contaminated and uncontaminated soils and venting these soils with air containing an inert tracer gas for a given period of time. The apparatus for the respiration test is illustrated in Figure 2. Each site had a cluster of three to four probes placed in the contaminated soil of the test location. A 1 to 3% concentration of inert gas (helium) was added to the air, which was injected for about 20 to 24 hours. The air provides oxygen to the soil, while inert gas measurements provide data on the diffusion of O_2 from the ground surface and the surrounding soil and assure that the soil gas sampling system does not leak. The background control location was placed in an uncontaminated site with air injection to monitor natural background respiration.

Measurements of CO_2 and O_2 concentrations in the soil gas were taken before any air and inert gas injection. After air and inert gas injection was turned off, CO_2 , O_2 , and inert gas concentrations were

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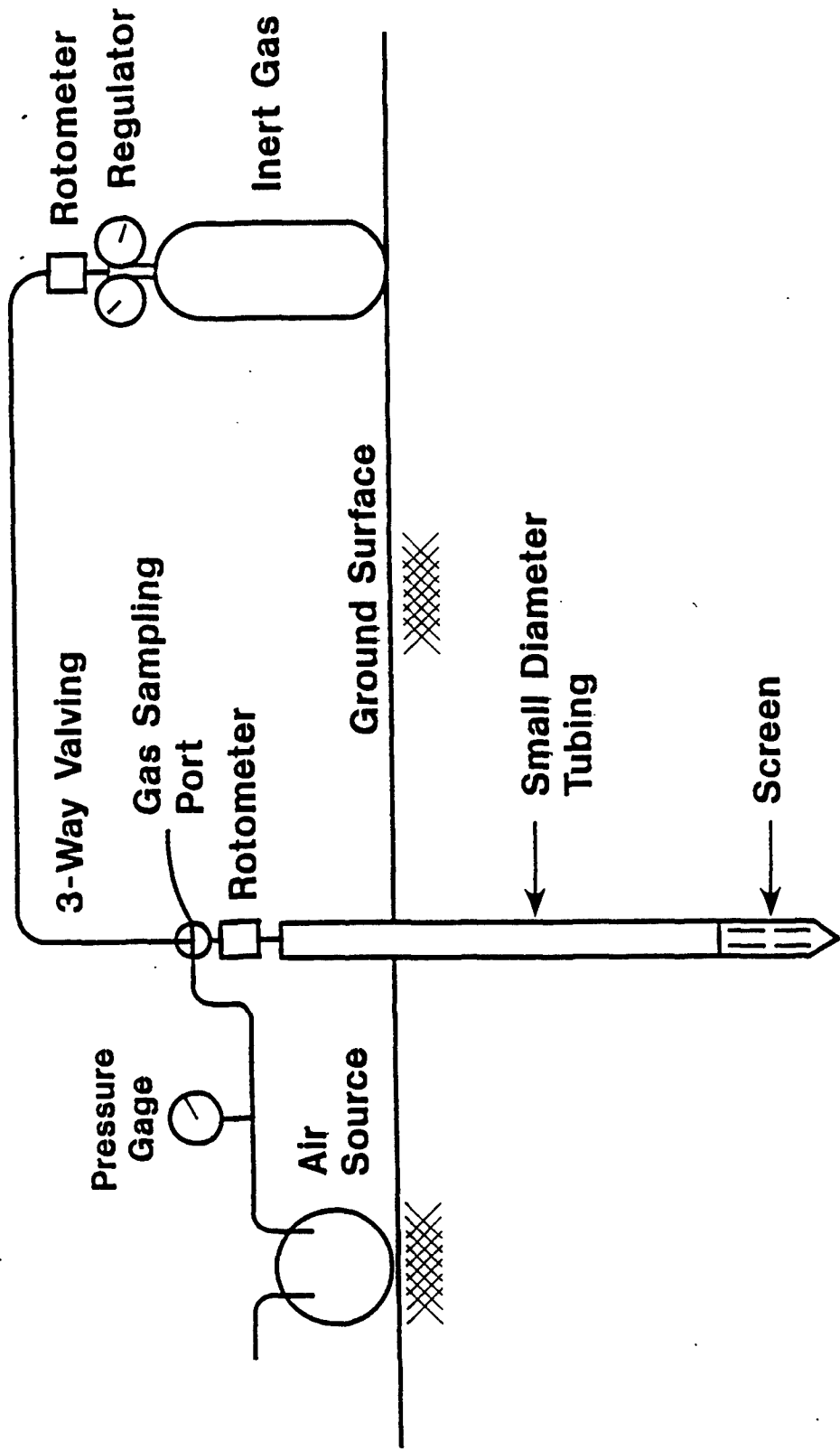


Figure 2. In Situ Respiration Test Apparatus.

monitored over time. Before a reading was taken, the probe was purged a few times until the CO_2 and O_2 readings were constant. Initial readings were taken every 2 hours and then progressively over 4- to 8-hour intervals. The experiment was usually terminated when the O_2 concentration of the soil gas was $\sim 5\%$. A detailed description of the in situ respiration test procedure is presented in Hinchee et al.¹²

Oxygen utilization and carbon dioxide production rates were used to estimate biodegradation rates, expressed in milligrams of hexane-equivalent/kilograms of soil per day. Inorganic uptake of O_2 was assumed to be negligible. Aerating the soil for 24 hours was assumed to be sufficient to oxidize any ferrous ions.

Carbon dioxide production proved to be a less useful measure of biodegradation than O_2 disappearance. The biodegradation rate in milligrams of hexane-equivalent/kilograms of soil per day based on CO_2 appearance is usually less than can be accounted for by the O_2 disappearance. In the case of the high pH and high alkalinity soils at Fallon NAS, little or no gaseous CO_2 production was measured. This could be due to the formation of carbonates from the gaseous evolution of CO_2 produced by biodegradation.

For the initial in situ respirometry measurements at Fallon, four gas monitoring probes were emplaced to depths of about 1.5 meters in clayey soil contaminated with JP-5; one background gas monitoring probe was emplaced in adjacent uncontaminated soil. Measurements of respiration rates during bioventing at Fallon are conducted using permanent soil gas probes installed in 23 sealed

boreholes at three depths (1, 2, and 3 meters) above the water table; two of these probes are located outside the contaminant plume. Three probes at Patuxent River were driven into sand to just above the groundwater table at depths of 4 to 6 meters. These served as test, gas control, and background gas sampling probes, respectively. Two permanent soil gas probes were monitored in each of three boreholes at Kaneohe Bay MCAS. Two boreholes were emplaced above the light, nonaqueous-phase liquid (LNAPL) plume and the soil gas probes in each borehole were situated just above the free product layer and just below the upper zone of contamination, respectively. The third borehole was situated outside the LNAPL plume. To date, in situ respiration testing has not been conducted at Twentynine Palms, CA.

C. Remedial Design: Fallon

The site at Fallon NAS was chosen for a demonstration of the bioslurping technology due to the presence of LNAPL on the shallow water table. The bioslurper technology is unique because it utilizes elements of two separate remedial technologies, **bioventing** and **free-product recovery**, to address two separate contaminant media. Both technologies are widely used in some form.

Bioslurping combines elements of each to simultaneously recover free product and aerate vadose zone soils, thus enhancing the capabilities of each used alone. Conventional FPR skimmer systems generally are inefficient for FPR because they have little effect on free product outside the recovery well, so efficiency relies on the passive movement of fuel into the recovery well. Dual-pump FPR systems increase recovery efficiency by drawing the water table down several feet to create a hydraulic gradient into the well. Although higher recovery rates are achieved, creation and maintenance of the hydraulic gradient can require extraction of large volumes of groundwater that must be

treated prior to discharge. In addition, lowering the water table may serve only to trap much of the free product beneath the water table when the water table returns to its normal level.

Bioslurping improves free-product recovery efficiency without requiring the extraction of large quantities of groundwater. The bioslurper system pulls a vacuum of 13 to 51 cm of mercury on the recovery well to create a pressure gradient to force movement of fuel into the well. The system is operated to cause negligible drawdown in the aquifer, thus reducing the problem of free-product entrapment.

Bioventing of the vadose zone soils is achieved by withdrawing soil gas from the recovery well. The slurping action of the bioslurper system cycles between recovering liquid (free product and/or groundwater) and soil gas. The rate of soil gas extraction is dependent on the recovery rate of liquid from the well system. When free-product removal activities are complete, the bioslurper system is easily converted to a conventional bioventing system to complete remediation of the vadose zone soils.

A total of 48 bioventing wells were installed for incorporation into the bioventing system at Fallon NAS (see Figure 3 for bioventing system layout). Wells were installed to an approximate depth of 4 m and were constructed of 5-cm-diameter Schedule 40 PVC with 2.1-m-long, 10-slot well screens. A medium-graded sand filter pack was installed across the screened interval. The rest of the annular space was plugged with a wetted bentonite chip plug to near surface followed by a concrete surface seal.

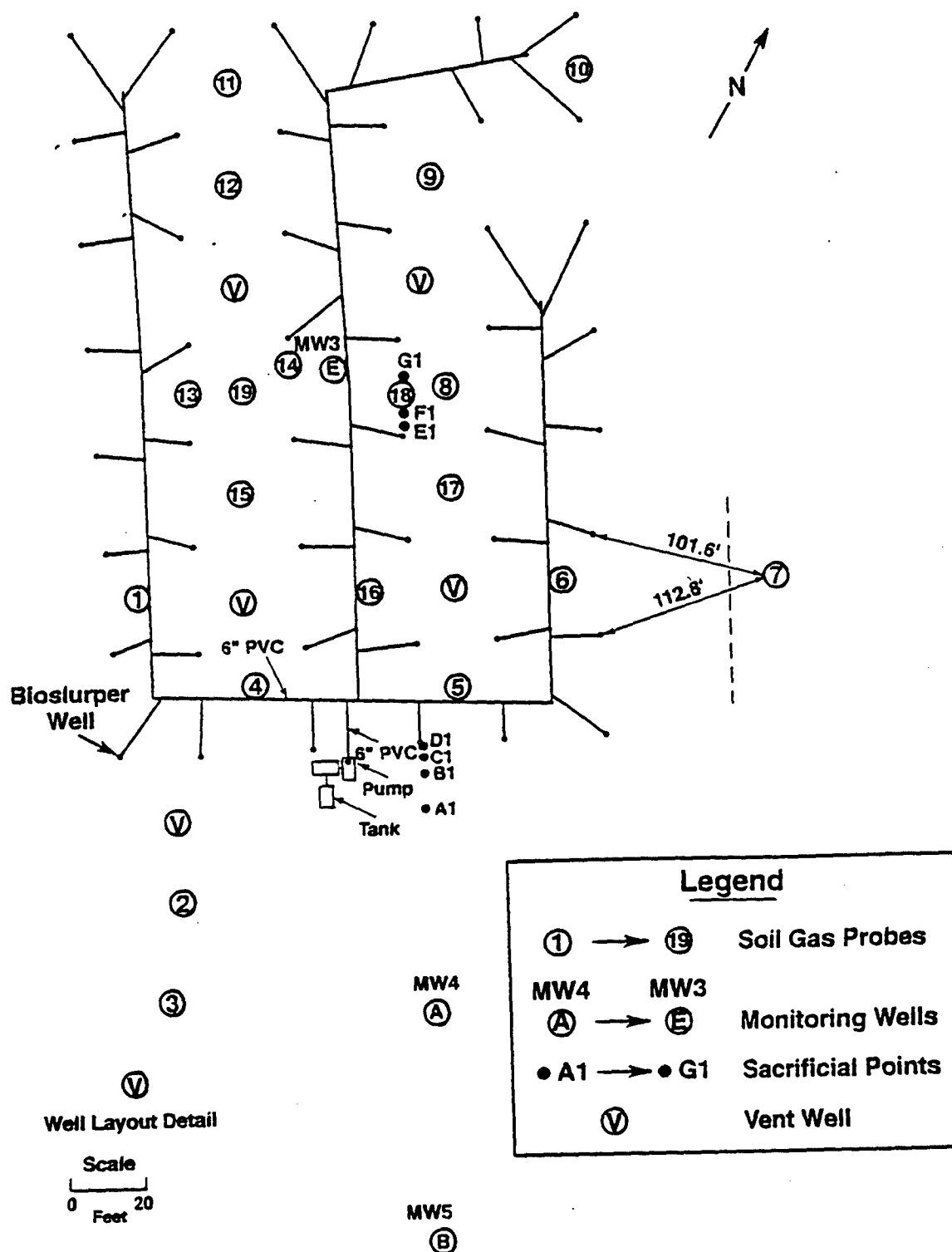


Figure 3. Fallon Naval Air Station - Bioventing System Layout.

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The system is designed to simultaneously vent the soils and skim free product from the water table. To accomplish this, a 2.5-cm-diameter PVC suction tube was inserted inside each well through a vacuum-tight well seal. The depth of the tube is adjustable to allow for selective withdrawal of water, free product, and/or soil vapor by placing the suction tube below, at, or above the water table surface, respectively. Each suction tube is tied into a larger diameter (10-cm and 15-cm) PVC pipe manifold. The suction tubes are valved to allow for variable flow adjustment, and an in-line sampling port allows for collection of the process fluids being removed from each well. Each well also has a vacuum release valve at the surface to allow for comparison of free-product recovery under vacuum and free-product recovery at atmospheric pressure. Under normal operating conditions the vacuum release valve is kept closed to allow for maximum bioventing. Figure 4 shows a diagram of a bioslurper well.

All of the bioslurper wells were connected through the PVC manifold to a 10-horsepower dewatering pump. The dewatering pump is capable of pumping water, free-phase petroleum, and soil gas from the wells. The liquid discharge from the pump is processed through an oil/water separator (OWS) to separate the aqueous from the petroleum phases. The OWS is connected to a 1,890-L steel tank for collection of free-phase petroleum. The tank is equipped with a float switch to shut off the dewatering pump when the tank is nearly full. Figure 5 shows a diagram of the OWS system components. The aqueous-phase discharge from the OWS (Megator Model Meg-S 24.60) is directed to a 529-L PVC tank that also has a float switch for overflow protection. A 5-horsepower irrigation pump directs the tank water to the Fallon NAS sanitary sewer. The OWS is rated for an aqueous discharge of 15 ppm total petroleum hydrocarbons and can operate at up to 95 L per minute.

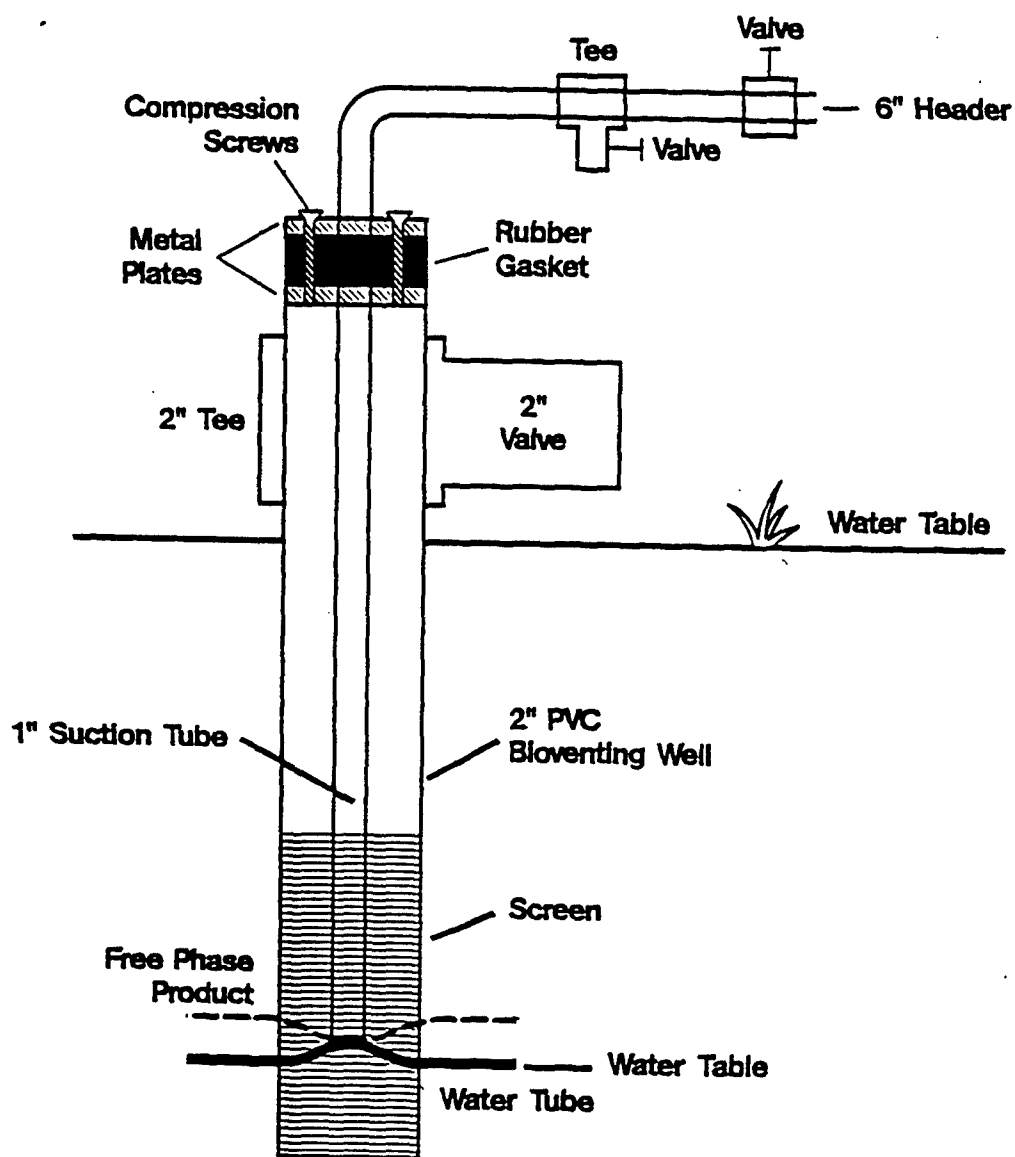


Figure 4. Bioslurper Well Design.

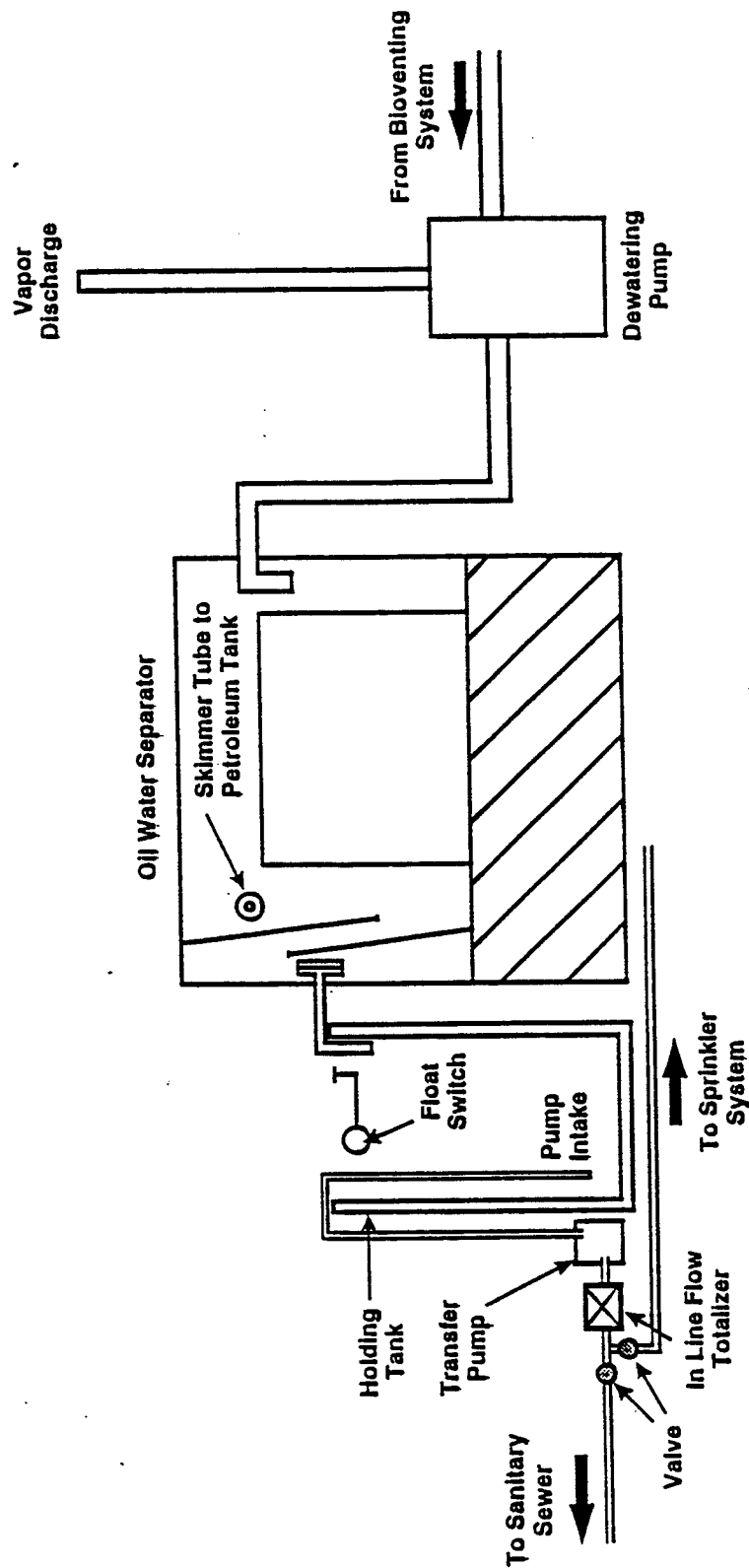


Figure 5. Diagram of Bioventing System Components. (not to scale)

The dewatering pump is fitted with a vacuum assembly through which the soil gas is vented to the open atmosphere under permit from the Nevada Department of Environmental Protection. Vapor is discharged through a 3-m-high, 5-cm-diameter polyvinyl chloride (PVC) stack.

V. RESULTS AND DISCUSSION OF LABORATORY TREATABILITY STUDIES

Figure 6 shows the results of laboratory studies using soil contaminated with JP-5 from Patuxent River that was diluted to different TPH concentrations with clean sterile sand. As seen in the figure, the lower fuel concentrations degraded rapidly, whereas soil concentrations of 830 and 1570 mg/kg appeared to change negligibly during the 4-month experiment, despite significant fluctuation in concentration among replicate bottles. In retrospect the total heterotrophic bacterial counts (colony-forming units, or CFUs) fluctuated minimally among soil samples having different initial TPH concentrations.

To evaluate the effect of initial TPH concentration on soil treatment, specific growth rates (Equation 1) and specific substrate utilization rates (Equation 2) were calculated for the logarithmic growth phase at each TPH concentration (triplicate vials of soil):

$$dX/dt = \mu X \quad (1)$$

$$-(dS/dt)/X = kS \quad (2)$$

where

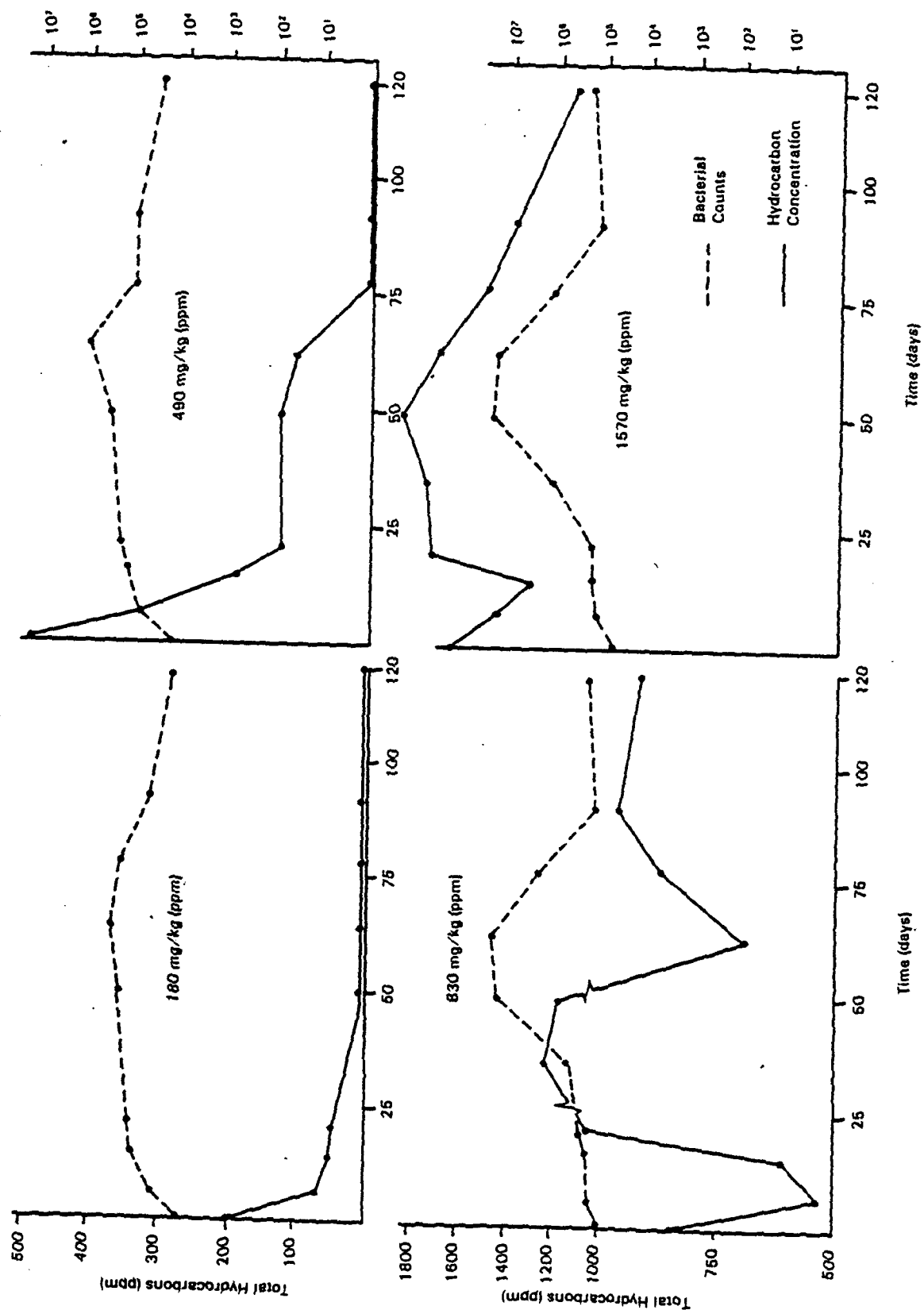


Figure 6. Effects of Hydrocarbon and Bacteria Concentrations in Sand on Hydrocarbon Degradation Rates.

dX/dt = microbial growth rate, CFU/g.d

μ = specific growth rate, day⁻¹

X = bacterial counts, CFU/g

$-(dS/dt)/X$ = specific substrate utilization rate,
(mg/d)/(CFU/g)

k = first-order rate constant, day⁻¹

S = substrate concentration, mg/kg.

Equation 2 is applied only in continuous-flow stirred reactors in which steady-state substrate and biomass concentrations are established. In the batch systems used in the experiments, the specific substrate utilization rate may be approximated by normalizing k to the biomass concentration. Because biomass increased during the batch experiments, k was normalized using the mean X during the logarithmic growth phase. Estimated specific substrate utilization rates therefore are reported as $k/X(\text{day}^{-1}/\text{CFU/g})$.

Specific growth rates and estimated specific substrate utilization rates for the four initial soil TPH concentrations are listed in Table 1. Factorial design analysis of variance (ANOVA) showed that the population means for the four specific growth rates were not significantly different ($\alpha \leq 0.05$). However, ANOVA analysis showed that the estimated specific substrate utilization rates declined as a function of initial TPH concentration ($\alpha \leq 0.05$).

Table 1. Logarithmic-phase Specific Growth Rates and Estimated Specific Utilization Rates for Four Initial TPH Concentrations

| TPH Concentration (mg/kg) | Specific Growth Rate (day⁻¹) | Specific Estimated Substrate Utilization Rate (day⁻¹/CFU/g) |
|--------------------------------------|--|---|
| 180 | 0.407 | 1.03×10^{-6} |
| 490 | 0.052 | 5.4×10^{-7} |
| 830 | 0.093 | 0 |
| 1,570 | 0.111 | 0 |

The concentration effect exhibited by TPH concentrations at or greater than 830 mg/kg in these experiments should not have been limited by dissolved oxygen, pH or nutrients. The dissolved oxygen concentrations in the soil systems were maintained at ≥ 3 mg/L, and the pH was maintained between 6.5 and 7.0. The concentrations of the two primary nutrient additions, $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$, decreased negligibly during the 120-day treatment. The results indicate that low degradation rates observed with the higher soil TPH concentrations may be due to surface area and bioavailability phenomena. Bacteria may not be physically capable of degrading significant water-immiscible hydrocarbons when present at high concentrations, when the substrate exists as large globules that are poorly accessible to biosurfactants.^{13,14}

To evaluate the potential of stimulating the biodegradation of petroleum with TPH concentrations above 830 mg/kg, a vial containing soil contaminated with 2,000 mg/kg TPH was amended with 10 mg/L methanol, mixed with the original soil-water solution. This methanol addition was repeated weekly over the 34-day treatment period. Figure 7 shows that the methanol amendment resulted in a significant loss of TPH, amounting to 83% over the experimental period. The specific growth rate and the estimated specific substrate utilization rate for the methanol-amended system were 0.87 day^{-1} and $2.28 \times 10^{-5} \text{ day}^{-1}/(\text{CFU/g})$, respectively. By factorial ANOVA, these values are significantly greater than the specific growth rates and estimated specific substrate utilization rates for the 830 and 1,570 mg/kg TPH experiments.

Although the results of the experiment with methanol addition were confounded by a lack of decline in bacterial counts over the shorter experimental period and a much higher specific growth rate, the most logical reason for increased hydrocarbon biodegradation rate is the hydrocarbon solubilization

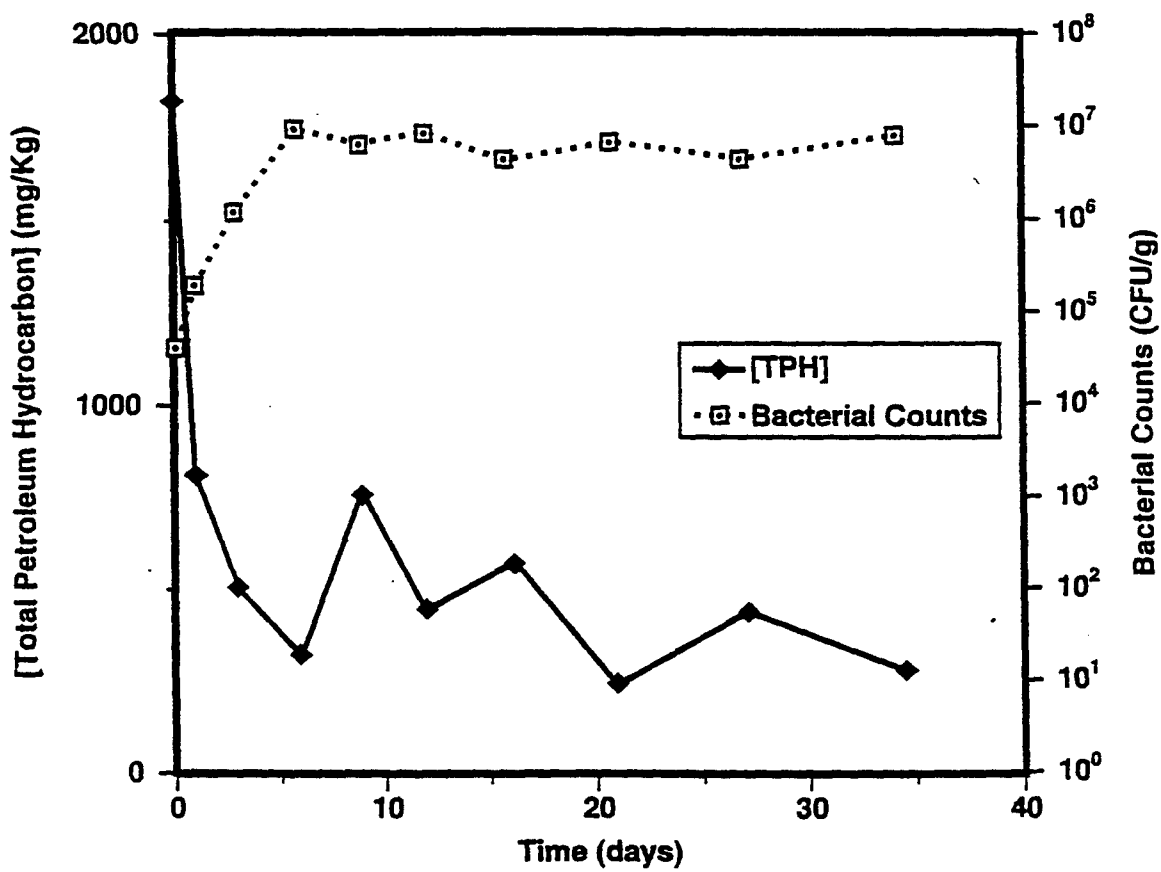


Figure 7. Biodegradation and Bacterial Counts During Treatment with Methanol Amendment.

effect promoted by a water-soluble cosolvent such as methanol. The result would be greater bioavailability of the water-immiscible hydrocarbon compounds. Because the experimental vials were continually agitated, the solubilization effect experienced would be much greater than what should be expected in an in situ treatment system, however. Thus these results serve mainly to help define the problem rather than to provide a practical solution.

VI. RESULTS AND DISCUSSION OF FIELD STUDIES

A. In Situ Respiration Testing

i. Fallon Naval Air Station, NV

The in situ respiration test at Fallon NAS was performed in the summer of 1990. The observed biodegradation rates ranged from 4.4 to 5.9 mg/kg day as hexane (based on oxygen utilization rates). Carbon dioxide production was not significant during the test.

ii. Patuxent River Naval Air Station, MD

The in situ respiration test at Patuxent River NAS was performed in the summer of 1990. The observed biodegradation rate was 2.9 mg/kg day as hexane (based on oxygen utilization rate). Carbon dioxide production indicated a biodegradation rate of 1.5 mg/kg day. Detailed descriptions of the respiration tests at Fallon and Patuxent River NAS are described elsewhere.¹⁵

iii. Kaneohe Bay MCAS, HI

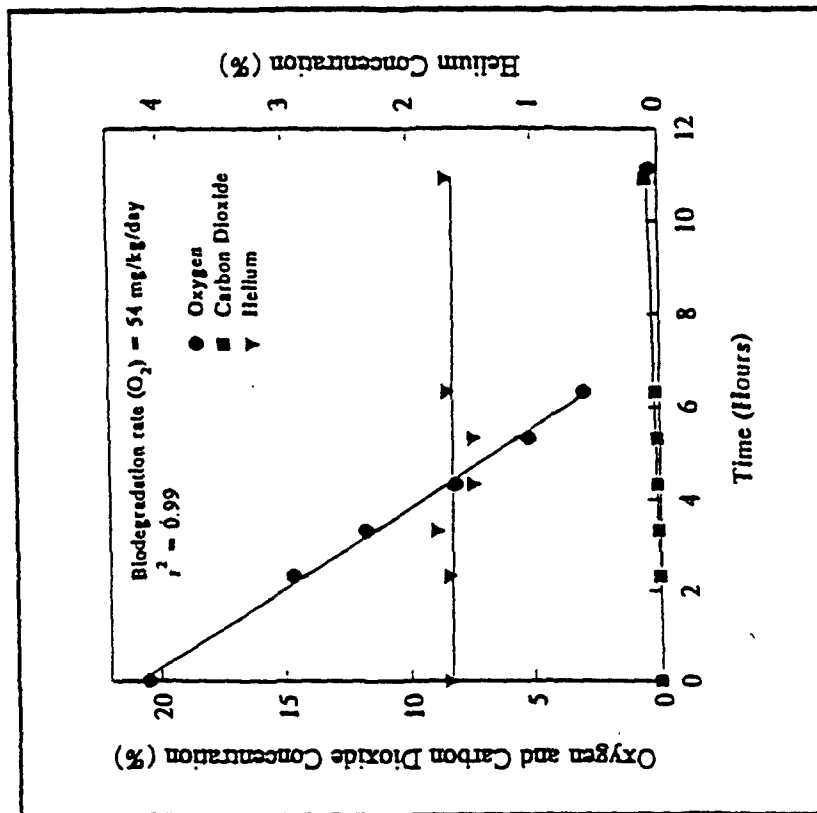
The in situ respiration test at the Kaneohe Bay MCAS was performed in the summer of 1993. Two sequential respiration tests were performed. The first test was performed on August 3, 1993 according to the standard protocol procedure with air injection being performed for 20 hours. Soil

gas was sampled for oxygen, carbon dioxide, and hydrocarbon concentrations. Oxygen depletion was extremely rapid, with all monitoring points in the contaminated zone reducing from more than 18% to less than 5% in less than 4 hours. The helium tracer concentration held constant during the test, indicating the leakage and diffusion were insignificant. Carbon dioxide production was insignificant. The background probe indicated very little oxygen depletion during the test.

Due to a concern that the high chemical oxygen demand at this site might be contributing to oxygen depletion, it was decided to run a second test at the same monitoring points beginning on August 6, 1993. Air and inert tracer (helium 1 to 2%) were injected for an additional 44 hours, and soil gas monitoring was conducted as in the first experiment. Oxygen depletion was slower than in the first experiment, with all monitoring points in the contaminated zone reducing from more than 19% to less than 5% in less than 12 hours. The helium tracer concentration held constant during the test, indicating the leakage and diffusion were insignificant. Carbon dioxide production again was insignificant. The background probe indicated very little oxygen depletion during the test. See Figure 8 for in situ respiration data for one monitoring point during each test.

The biodegradation rates observed ranged from 60 to 122 mg/kg day as hexane (based on oxygen utilization rate) for the first test and 22 to 105 mg/kg day for the second test. Carbon dioxide production was insignificant at all points. Table 2 presents data for both Kaneohe respiration tests from one soil gas monitoring point. Figure 9 presents oxygen utilization rates for all three in situ respiration test sites.

MPB - (6' - 8')
8/6/93



MPB - (6' - 8')
8/3/93

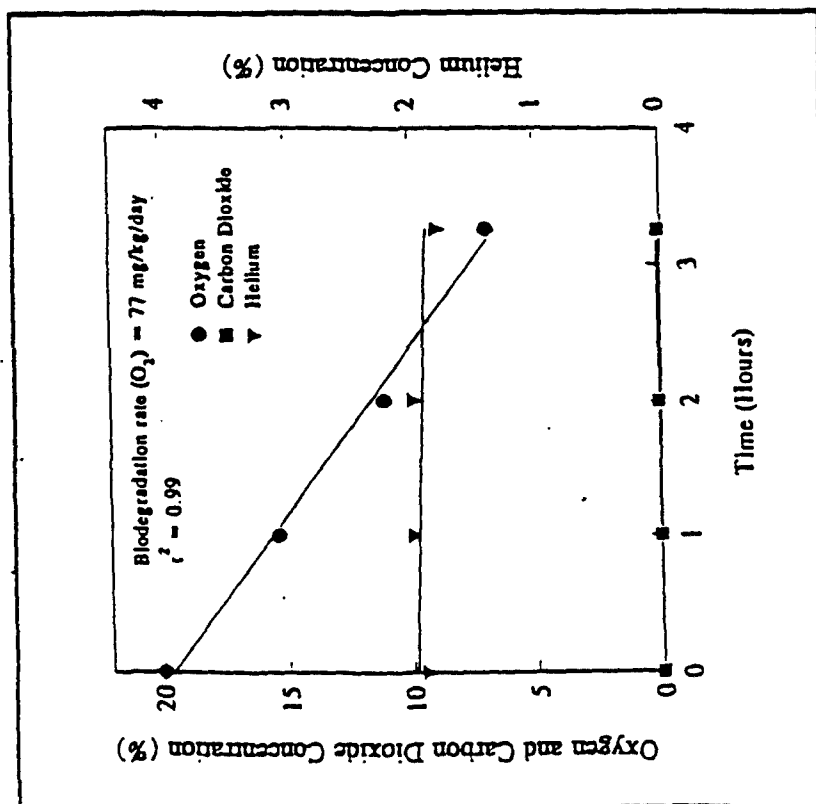


Figure 8. Kaneohe Bay Marine Corps Air Station - In Situ Respiration Data.

Table 2. Kaneohe Bay Marine Corps Air Station - In Situ Respiration Data

| Kaneohe O ₂ Utilization | | | | |
|------------------------------------|----------------------------------|--------|---------------------------------|--------|
| Monitoring Point | Oxygen Utilization Rate (%/hour) | | Biodegradation Rate (mg/kg/day) | |
| Test Date | 8/3/93 | 8/6/93 | 8/3/93 | 8/6/93 |
| Background | 0.06 | 0.06 | 1.2 | 1.2 |
| MPA (2.3 - 2.6 m) | 3.1 | 1.1 | 60 | 22 |
| MPA (1.5 - 1.8 m) | 4.1 | NS | 78 | NS |
| MPB (3.8 - 4.9 m) | 6.4 | 5.5 | 122 | 105 |
| MPB (1.8 - 2.4 m) | 4 | 2.8 | 77 | 54 |

NS = No Sample Taken

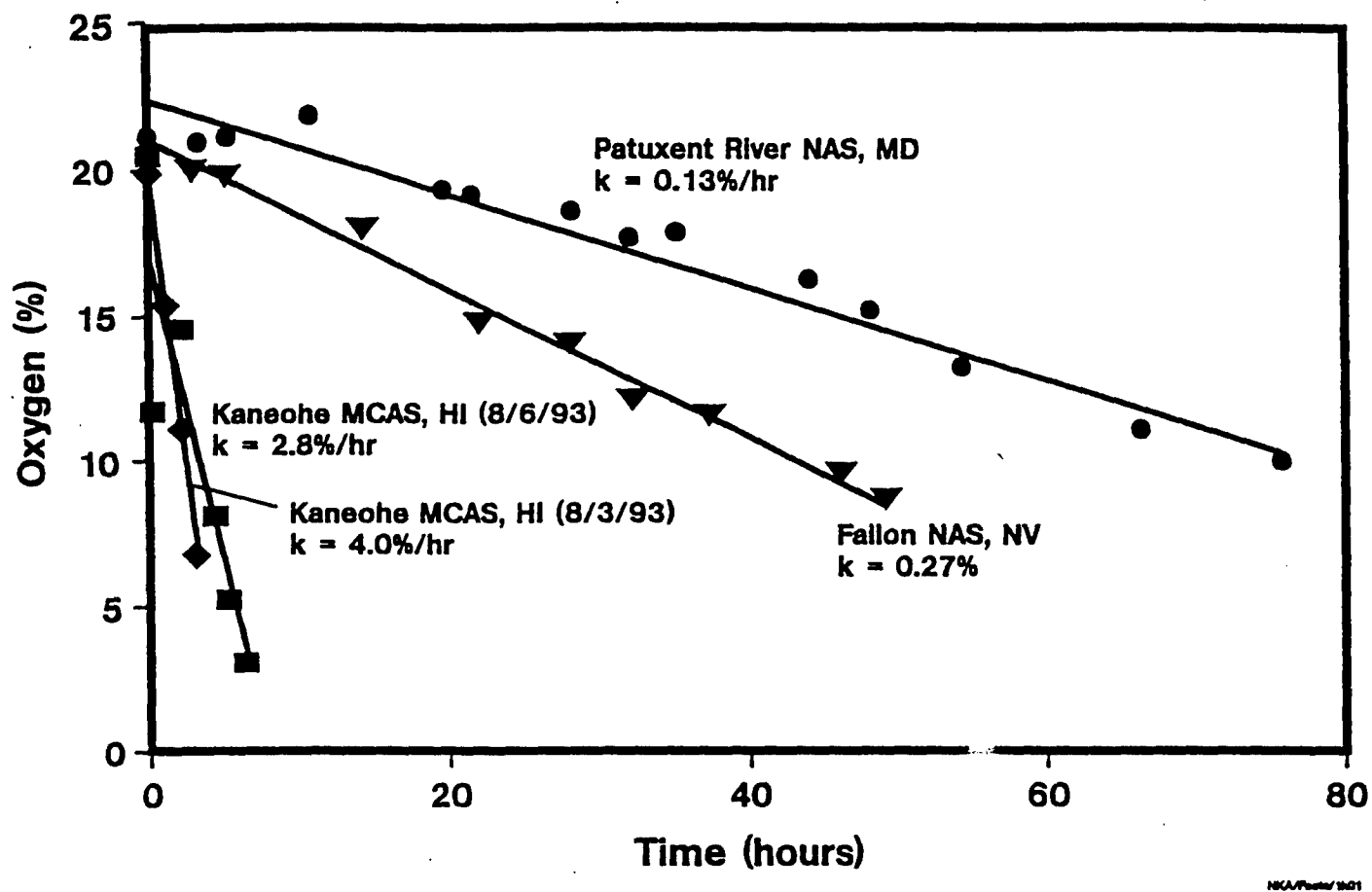


Figure 9. Oxygen Utilization Rates Measured at Three Test Sites.

B. Air Permeability Testing - Twentynine Palms, MCAGCC, CA

At the Twentynine Palms study site a permeability test was conducted at site 17 Alpha. The test was conducted by injecting air into a single vent well (screened from 19.8 to 0.9 meters) until pressure in the soil gas monitoring points stabilized (approximately 20 minutes). The air injection rate and pressure were approximately $4.5 \text{ m}^3 \text{ min}^{-1}$ and 66 cm of water, respectively. The gasoline-powered blower was operated at approximately 1,830 rpm. Soil gas pressures were monitored at all screened intervals of three multi-level screened soil gas monitoring points. Monitoring points (MP) were placed at 55.2 (MP-D), 24.4 (MP-F), and 5.2 (MP-E) meters from the vent well. MP-D is screened at depths of 7.6, 15.2, 22.8, 30.4, 39.5, 48.6, 54.7, and 60.8 meters. MP-E is screened at depths of 1.5, 3.0, 4.6, 6.1, 9.1, 12.2, 15.2, and 18.2 meters. MP-F is screened at depths of 3.0, 6.1, 9.1, 12.2, and 8.2 meters.

The results of the soil gas permeability test conducted at the Twentynine Palms site have indicated that the radius of influence (R_f) is approximately 49 m. The permeability (K) of the soil was estimated to be approximately 18 darcys which is typical for medium to coarse sands as observed on the site.

C. Soil Gas Analysis - Twentynine Palms MCAGCC, CA

Results of soil gas analyses conducted at monitoring points 17A-MP-H and 17A-MP-E are shown in Tables 3 and 4, respectively. Although total petroleum hydrocarbon (TPH) levels at both sites are similar, with concentrations ranging from 240 to 1,480 ppm, oxygen levels at 17A-MP-H are considerably lower than levels observed at 17-MP-E. Typically, oxygen levels below 5% would indicate that the soils are oxygen deficient and are favorable for remediation by bioventing. The

Table 3. Soil Gas Data - Twentynine Palms MCAGCC

| 17A-MP-H | | | | | | |
|--------------|--------------------|---------------------|-----------|--------------------|---------------------|-----------|
| Depth (m) | June 16, 1993 | | | July 16, 1993 | | |
| | O ₂ (%) | CO ₂ (%) | TPH (ppm) | O ₂ (%) | CO ₂ (%) | TPH (ppm) |
| 3.0 | 0 | 20 | 280 | 7 | 12 | 580 |
| 6.1 | 0 | 20 | 380 | 0 | 20 | 660 |
| 9.1 | 0 | 19 | 460 | 0 | 18 | 860 |
| 12.2 | 0.2 | 18 | 440 | 0.5 | 17 | 1000 |
| 15.2 | 0.3 | 18 | 490 | 0.9 | 17 | 1040 |
| 18.2 | 2 | 17 | 470 | 3 | 16 | 960 |
| 21.3 | 3 | 16 | 410 | 3 | 15 | 880 |

Table 4. Soil Gas Data - Twentynine Palms MCAGCC

| 17A-MP-E | | | | | | |
|--------------|--------------------|---------------------|-----------|--------------------|---------------------|-----------|
| Depth (m) | June 16, 1993 | | | July 16, 1993 | | |
| | O ₂ (%) | CO ₂ (%) | TPH (ppm) | O ₂ (%) | CO ₂ (%) | TPH (ppm) |
| 1.5 | 17 | 2 | 470 | 19 | 0.8 | 240 |
| 3.0 | 14 | 4 | 900 | 17 | 3 | 920 |
| 4.6 | 11 | 6 | 1010 | 13 | 6 | 1200 |
| 6.1 | 9 | 7 | 720 | 10 | 7 | 1200 |
| 9.1 | 5 | 11 | 710 | 6 | 11 | 1440 |
| 12.2 | 6 | 10 | 720 | 6 | 11 | 1400 |
| 15.2 | 8 | 8 | 720 | 9 | 8 | 1480 |
| 18.2 | 9 | 7 | 640 | 9 | 8 | 1340 |

elevated oxygen levels observed at 17-MP-E could suggest that factors other than oxygen concentration are limiting biodegradation in some areas. Other factors that could be limiting biodegradation include moisture deficiency and nutrient deficiency. Future studies will be conducted to identify limiting factors, and bioventing systems will be designed to compensate for site-specific limiting factors (i.e., moisture addition and/or nutrient addition, as appropriate).

D. Bioslurper System Operation - Fallon NAS, NV

The 0.4-hectare study site at Fallon NAS is located in an open field just downgradient from the JP-5 fuel supply pipeline for the NAS fuel farm (see Figure 1). The site was selected because of the large LNAPL plume and lack of structures in the vicinity, and to avoid planned construction activities at the in situ respiration test site studied in 1990. Full-scale startup of the bioslurper system was initiated in January 1993. Process monitoring includes tracking the mass of hydrocarbons removed in liquid, gaseous, and dissolved form, and monitoring the mass of hydrocarbons remediated via in situ biodegradation. The mass of free-phase fuel recovered is measured daily. The OWS aqueous discharge is sampled monthly and is analyzed for TPH. Stack vapor discharge is sampled and analyzed for TPH using field instrumentation daily and is sent to a laboratory for analysis quarterly. The TPH concentration in the aqueous effluent has ranged from 50 to 130 ppm. The mass of hydrocarbons emitted from the bioslurper system vapor discharge averages approximately 2.3 kg per day.

The bioslurper system is being operated to maximize fuel recovery while minimizing the volume of groundwater that must be extracted. Average FPR rates have ranged from 25 gallons/day (gpd) to 7 gpd, whereas groundwater extraction rates have ranged from 0.5 to 0.3 gallon per minute (gpm).

Figure 10 presents the free product and groundwater recovery data for the bioslurper system from full-scale startup to date.

The bioslurper test site is located approximately 150 meters from the site where initial in situ respiration testing was conducted. Most soil gas monitoring points within the test site have measured very low respiration rates, with O_2 concentration of 15 to 19% observed 3 months after soil gas probe emplacement. This contrasts with the respiration rates made 18 months earlier at the fuel farm (see Figure 9).

It appears that biodegradation at the test site is being inhibited by some factor other than oxygen deficiency. Free fuel is trapped in a narrow soil zone, confined beneath a silt layer. This excessive fuel concentration could be the major limiting factor. The JP-5 release is very fresh, making it possible that the microbial population has not had time to adapt to the fuel. Corrosion inhibitors in the fuel may also be inhibiting microbial activity. Oxygen-deficient conditions have been observed just 30 meters from the bioslurper study site. A soluble hydrocarbon plume from gasoline contamination may be influencing respiration rates in this area. Bench-scale laboratory studies are ongoing to determine the reason for the observed poor respiration rates at the bioslurper test site, compared to sites displaying oxygen deficiency.

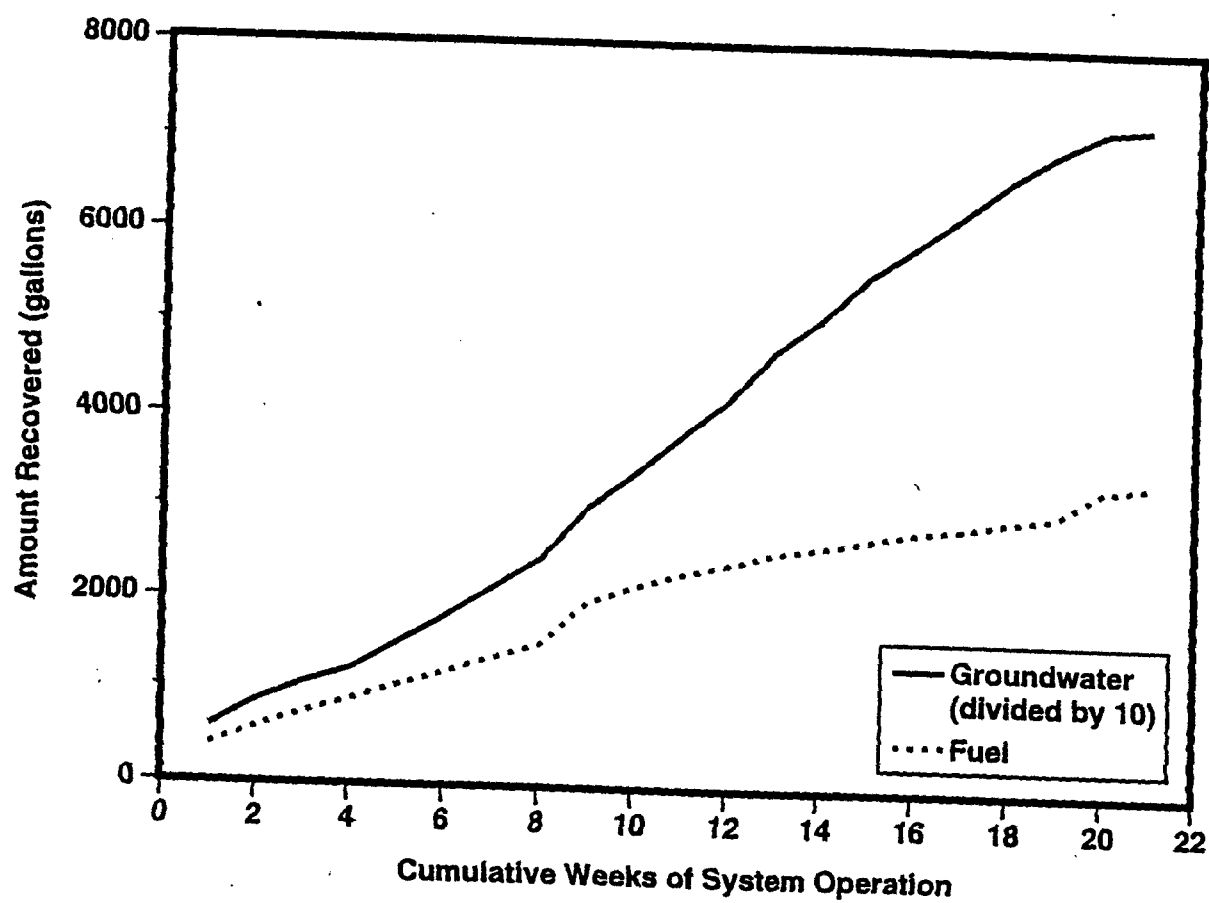


Figure 10. Free Product Recovery Data for NAS Fallon.

VII. FUTURE WORK

A. Fallon NAS, NV

FPR activities at the Fallon NAS site will continue until the fuel recovery rate approaches zero. The bioslurper system eventually will be converted to a conventional bioventing system to treat residual vadose zone contamination. At the completion of the study, final soil samples will be collected and analyzed for post-treatment characterization.

B. Kaneohe MCAS, HI

A full-scale bioslurper demonstration project is planned for the Kaneohe Bay site. Pretreatment site characterization will be conducted in the winter/spring 1994, and system installation is planned for mid-1994 to late 1994.

C. Twentynine Palms, CA

Site characterization and vent well/monitoring point installations will be continued through 1993 at Twentynine Palms. Pilot- and demonstration-scale bioventing projects will be initiated in late 1993. One area of immediate interest is further investigation of bioventing efficiency utilizing passive aeration, which will involve controlled movement of air into bioventing wells with changes in barometric pressure. Another area of interest is to evaluate the effect of soil moisture biodegradation rates and develop methods for deep irrigation of contaminated soil that is now essentially dry to enhance fuel bioremediation.

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